

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 628 433 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: **93904355.0**

(51) Int. Cl.⁵: **B43L 19/00**

(22) Date of filing: **26.02.93**

(86) International application number:
PCT/JP93/00239

(87) International publication number:
WO 93/16887 (02.09.93 93/21)

(30) Priority: **28.02.92 JP 78828/92**
27.08.92 JP 252282/92

(43) Date of publication of application:
14.12.94 Bulletin 94/50

(84) Designated Contracting States:
DE FR GB

(71) Applicant: **PENTEL KABUSHIKI KAISHA**
7-2, Nihonbashi Koamicho
Chuo-ku, Tokyo 103 (JP)

(72) Inventor: **TAKAHASHI, Yasuhiro**
202 Rose Corporation,
2-21-34, Takasago
Soka-shi, Saitama 340 (JP)

(74) Representative: **Lewin, John Harvey et al**
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) **ERASER.**

(57) An eraser excellent in erasing performance even when applied under a weak rubbing force, which is made from a chlorine-free styrenic or olefinic thermoplastic elastomer as the base material so that it can be incinerated without emitting any toxic chlorine-containing gas. The first embodiment thereof comprises a styrenic thermoplastic elastomer, an oily matter and a gelling agent. The second embodiment comprises a styrenic thermoplastic elastomer and a styrenic oligomer. The third embodiment comprises an olefinic thermoplastic elastomer and has a number of microvoids therein.

EP 0 628 433 A1

Technical Field

The present invention relates to an eraser for erasing handwriting written with a pencil or a mechanical pencil. In particular, the invention relates to an eraser excellent in erasing performance even when it is applied under a weak rubbing force like a polyvinyl chloride eraser, which can be incinerated without emitting any toxic chlorine-containing gas.

Background Art

Erasers leave refuse after being used. The base material of polyvinyl chloride erasers which have prevalently been used is polyvinyl chloride which is a compound that contains a large amount of chlorine. Therefore, when the refuse is incinerated, a toxic chlorine-containing gas is emitted to cause air pollution. On the contrary, thermoplastic elastomer erasers are very favorable, because they do not contain any chlorine compound and hence are free from the above problem. Among them, styrenic and olefinic elastomers are particularly suitable for use as the material of erasers, since they highly adsorb carbon powder constituting handwriting written with a pencil or a mechanical pencil to exhibit an excellent erasing performance.

However, when the styrenic or olefinic thermoplastic elastomer is used singly, it will not be abraded even when rubbed strongly, since it has a high breaking strength and thus it does not function as an eraser. Therefore, it is combined with a factice or resin usually incorporated into rubber-base erasers or with another thermoplastic elastomer to function as an eraser easy to be abraded.

However, even when the breaking strength of the eraser as a whole is lowered by the combination with the above-described substance to abrade it by rubbing, the breaking strength of the styrenic or olefinic thermoplastic elastomer per se is not lowered. Therefore, erasers comprising the styrenic or olefinic thermoplastic elastomer as the base material have a problem that the erasing performance under a weak rubbing force is far inferior to that of the polyvinyl chloride eraser.

Disclosure of Invention

An object of the present invention is to provide an eraser excellent in erasing performance even when used under a weak rubbing force, which comprises a styrenic or olefinic thermoplastic elastomer as the base material.

The first embodiment of the eraser of the present invention comprises a styrenic thermoplastic elastomer as a base material, 1 to 3 parts by weight, per part by weight of the base material, of an oily matter and a gelling agent.

The second embodiment of the eraser of the present invention comprises a styrenic thermoplastic elastomer as a base material and a styrenic oligomer.

The third embodiment of the eraser of the present invention comprises an olefinic thermoplastic elastomer as a base material and has a number of microvoids therein.

Best Mode for Carrying out the Invention

A detailed description on the present invention will now be made hereinbelow.

At the outset, a description will be made on the first embodiment of the present invention relating to an eraser which comprises a styrenic thermoplastic elastomer as the base material, an oily matter and a gelling agent.

The styrenic thermoplastic elastomer to be used as the base material is a triblock copolymer having molecule-constraining components (hard segments) for preventing plastic deformation and an elastic rubber component (soft segment) in the molecule, and having a structure in which the rubber component is sandwiched between the molecule-constraining components. At an ambient temperature, two or more molecule-constraining components at both ends of the molecule gather to form a domain to thereby yield a three-dimensional network structure like a crosslinked rubber. At a high temperature, the domain comprising the molecule-constraining components is plasticized to lose the power of constraining the molecule. Therefore, the styrenic thermoplastic elastomer exhibits the properties of a vulcanized rubber at the ambient temperature and is plasticized at a high temperature so that it can be molded on an ordinary plastic molding machine.

The styrenic thermoplastic elastomers include a styrene/butadiene/styrene copolymer wherein the molecule-constraining component is polystyrene (the same applied hereinbelow) and the rubber component

is polybutadiene; a styrene/isoprene/styrene copolymer wherein the rubber component is polyisoprene; a styrene/ethylenebutylene/styrene copolymer wherein the rubber component is polyethylenebutylene; and a styrene/ethylenepropylene/styrene copolymer wherein the rubber component is polyethylenepropylene.

Examples of commercially available styrenic thermoplastic elastomers will be given below. The styrene/butadiene/styrene copolymers include Tufprene A, Tufprene 125, 200, 315 and 912, Solprene T-406, T-411, T-414 and T-475, Asaprene T-420, T-430, T-431 and T-450 (products of Asahi Chemical Industry Co., Ltd.); and Cariflex TR1101, TR1102, TRKX138S, TR1118, TR1116, TR1184, TR1186, TR1122, TR4113, TR4122, TR4205, TR4260 and TR4261 and Kraton D1300 (products of Shell Kagaku K.K.). The styrene/isoprene/styrene copolymers include Cariflex TR1107, TR1111, TR1112 and TR1117 (products of Shell Kagaku K.K.). The styrene/ethylenebutylene/styrene copolymers include Tuftec H1052, H1041 and H1051 (products of Asahi Chemical Industry Co., Ltd.); Kraton G1650, G1652 and G1657X (products of Shell Kagaku K.K.); and Rabalon SJ4400, SJ5400, SJ6400, SJ7400, SJ8400, SJ9400, SE5400, SE6400, SS6400, SS7400, SS9400, MJ4300, MJ6300 and ME6301 (products of Mitsubishi Petrochemical Co., Ltd.). The styrene/ethylenepropylene/styrene copolymers include Septon 2002, 2003, 2023, 2043, 2063, 2005, 2006, 2103, 2104, 2105 and 4055 (products of Kuraray Co., Ltd.). Solprene T-475 contains 50 parts by weight of a naphthenic oil per 100 parts by weight of the styrene/butadiene/styrene copolymer. These styrenic thermoplastic elastomers may be used either singly or in combination of two or more of them.

It is also possible to lower the breaking strength of the styrenic thermoplastic elastomer by using a diblock copolymer which is a kind of the styrenic thermoplastic elastomer and which comprises a molecule-constraining component and a rubber component in combination with the above-described styrenic thermoplastic elastomer comprising the triblock copolymer as the base material. Examples of the diblock copolymers include Kraton G1726X (a product of Shell Kagaku K.K.) comprising 70% by weight of styrene/ethylenebutylene diblock copolymer and 30% by weight of styrene/ethylenebutylene/styrene triblock copolymer; and Kraton G1701X (a product of Shell Kagaku K.K.) which is styrene/ethylenepropylene diblock copolymer; and Septon 1001 and 1050 (products of Kuraray Co., Ltd.). When the diblock copolymer is used in combination, the amount thereof is desirably not larger than 30% by weight based on the whole styrenic thermoplastic elastomer. This is because when the amount of the diblock copolymer is larger than 30% by weight, the styrenic thermoplastic elastomer is apt to be plasticized or brought to a solution state at ambient temperature by an oily matter which will be described below.

The oily matter is used for reducing the breaking strength of the styrenic thermoplastic elastomer used as the base material. The oily matters include petroleum oils and liquid polymers.

The petroleum oils include paraffinic oils, naphthenic oils and aromatic oils derived from petroleums, and mixtures of them. Examples of known petroleum oils include not only extender oils for oil rubbers and process oils for compound, but also liquid paraffins, spindle oils and machine oils. The liquid paraffins include industrial liquid paraffins according to JIS K 2231 and those standardized by The Pharmacopoeia of Japan and Food Hygiene Law. Examples of those meeting the standards include Crystol 52, 70, 72, 102, 142, 172, 202, 262, 322 and 352 (products of Esso Sekiyu K.K.); and DN. Oil CP15N, CP32N, CP38N, CP68N, KP8, KP15, KP32, KP68 and KP100 (products of Idemitsu Kosan Co., Ltd.).

The petroleum oils can be classified according to Kurtz's classification into paraffinic oils wherein the number of carbon atoms in the paraffin chain accounts for at least 50% of the total number of the carbon atoms, naphthenic oils wherein the number of carbon atoms in the naphthene ring accounts for 30 to 45%, and aromatic oils wherein the number of carbon atoms in the aromatic ring accounts for at least 35%. The paraffinic oils include DIANA PX-32, PX-90, PW-32, PW-90, PW-380, PS-32, PS-90 and PS-430 (products of Idemitsu Kosan Co., Ltd.); and Shellflex 210, 310, 790, 1210 and 1310, Lubeflex 26, 100 and 460 (products of Shell Kagaku K.K.); Kyoseki Process P200, P300, P500 and Kyoseki EPT750 (products of Kyodo Oil Co., Ltd.). The naphthenic oils include DIANA NS-24, NS-100, NM-26, NM-280, NP-24, NU-80 and NF-90 (products of Idemitsu Kosan Co., Ltd.); Shellflex 371JY, 371N, 451, N-40, 22, 22R, 32R, 100R, 100S, 100SA, 220RS, 220S, 260, 320R and 680 (products of Shell Kagaku K.K.); and Kyoseki Process R25, R50, R200 and R1000 (products of Kyodo Oil Co., Ltd.). The aromatic oils include DIANA AC-12, AC-460, AH-16 and AH-58 (products of Idemitsu Kosan Co., Ltd.); Dutrex 729UK and 739 (products of Shell Kagaku K.K.); and Kyoseki Process X50 and X140 (products of Kyodo Oil Co., Ltd.).

Among the above-described petroleum oils, the paraffinic and naphthenic oils may be used either singly or in the form of a mixture of two or more of them, but the aromatic oils must be used in combination with the paraffinic oil and/or naphthenic oil. This is because when the number of carbon atoms in the aromatic rings accounts for 35% or above of the total number of the carbon atoms in the petroleum oil, the styrene domain in the styrenic thermoplastic elastomer is dissolved because of a high solubility of the polystyrene in the aromatic ring component, and the styrenic thermoplastic elastomer is plasticized or brought to a solution state at room temperature to make the production of the eraser impossible. Therefore, the number

of the aromatic carbon atoms in the petroleum oils must be below 35% of the total number of the carbon atoms.

The liquid polymers include liquid polyisoprenes, liquid polybutadienes and liquid polybutenes. The liquid polybutenes include Nisseki Polybutene LV-5, LV-10, LV-25, LV-50, LV-100 and HV-15 (products of Nippon Petrochemical Co., Ltd.); and Idemitsu Polybutene 0H, 5H, 10H, 15H, 0R and 15R (products of Idemitsu Petrochemical Co., Ltd.).

The oily matter must be used in an amount of 1 to 3 parts by weight per part by weight of the styrenic thermoplastic elastomer. When the amount thereof is smaller, the lowering of the breaking strength is insufficient and no satisfactory erasing performance can be achieved when the eraser is used under a weak rubbing force. On the contrary, when the amount of the oily matter is larger, the breaking strength of the elastomer is too low to achieve the erasing performance.

The gelling agent is used for inhibiting the so-called blooming wherein the oily matter oozes out to the eraser surface and also for preventing the hand or paper surface from staining at the time of using the eraser. The gelling agents usable herein include organic gelling agents such as dibenzylidenesorbitol, tribenzylidenesorbitol, dextrin/fatty acid esters, N-acyl fatty acid amides and castor oil derivatives; and inorganic gelling agents such as silica, bentonite and hectorite. Since silica has a particularly remarkable effect, it is preferred. The silica is, for example, Aerosil (a product of Nippon Aerosil Co., Ltd.) produced by the dry method, or Mizukasil (a product of Mizusawa Industrial Chemicals, Ltd.) or Nipsil (a product of Nippon Silica Industrial Co., Ltd.) produced by the wet method.

The gelling agent is used in an amount of preferably 0.1 to 10% by weight based on the oily matter. When the amount thereof is below this range, the remarkable effect is not always obtained and, on the contrary, when it is above this range, an adverse effect tends to be exerted on other properties of the eraser.

If necessary, chlorine-free thermoplastic resins other than the styrenic thermoplastic elastomers, and olefinic, ester and urethane thermoplastic elastomers can be used in addition to the above-described indispensable components. The amount of the styrenic thermoplastic elastomer is at least 25% by weight, preferably at least 50% by weight, based on the whole base material. Further, additives ordinarily contained in eraser, such as a filler, stabilizer, colorant and antifungal and antimicrobial agent are suitably usable. The fillers include calcium carbonate, magnesium carbonate, diatomaceous earth, clay, and fibrous or needle-like fillers for improving the bending strength, such as potassium titanate fibers, magnesium sulfate fibers, silicon nitride whiskers and silicon carbide whiskers. The stabilizers include antioxidants such as hindered phenols, ultraviolet absorbers such as benzotriazoles and oxalic acid anilides, and ultraviolet stabilizers such as hindered amines. The colorants include organic and inorganic pigments. The antifungal and antimicrobial agents include 2-(4-thiazolyl)-benzimidazole, zinc 2-pyridinethiol-1-oxide, metallic silver supported by calcium phosphate carrier and zinc antimicrobial agents.

The eraser can be produced by kneading the above-described components on an ordinary heating-type mixer such as a heating two-roller mill, pressure kneader or Banbury mixer and then molding the resultant blend on a molding machine such as a pressing machine, injection-molding machine or extruder.

The eraser of the above-described first embodiment of the present invention exhibits an excellent erasing performance even when it is used under a weak rubbing force, since the oily matter contained therein in an amount of 1 to 3 parts by weight per part by weight of the base material reduces the breaking strength of the styrenic thermoplastic elastomer used as the base material. Further, the oily matter does not ooze out to the eraser surface, since the gelling agent fixes the oily matter in the eraser by gelling. In addition, the blooming-inhibiting effect of the gelling agent is far superior to that of the fillers such as calcium carbonate and, therefore, only a small amount of the gelling agent will suffice for exhibiting its effect. Thus, the properties of the eraser are not so deteriorated as compared with the case of inhibiting the blooming with the filler.

Next, a description will be made on the second embodiment of the present invention, i.e. an eraser comprising a styrenic thermoplastic elastomer as the base material and a styrenic oligomer.

The styrenic thermoplastic elastomers to be used as the base material are the same as those described above with reference to the first embodiment.

The styrenic oligomer is used in order to weaken the breaking strength of the styrenic thermoplastic elastomer per se, to improve the erasing performance even when the eraser is used under a weak rubbing force, and to fine the textures of the abrasion surface of the eraser and the refuse thereof. The styrene oligomers used in the present invention are styrene resins having an average molecular weight of 100,000 or below, such as polystyrene, styrene/acrylic copolymer and α -methylstyrene.

Examples of commercially available styrene oligomers will now be described. The polystyrenes include Piccolastic A5 (average molecular weight: about 300), A75 (do.: about 900), D125 (do.: about 53000) and

D150 (do.: about 80000), and Endex 155 (do.: about 6200) (products of Rika-Hercules Inc.); Himer ST-95 (do.: about 10000) and ST-120 (do.: about 20000) (products of Sanyo Chemical Industrial, Ltd.). The styrene/acrylic copolymers include Himer SBM-100 (do.: about 15000), SBM-73 (do.: about 40000), SBM-3700 (do.: about 50000), SBM-600 (do.: about 60000), SBM-700 (do.: about 70000) and SEH-82 (do.: about 50000) (products of Sanyo Chemical Industrial, Ltd.). α -Methylstyrenes include Kristalex 3100 (do.: about 1000), 1120 (do.: about 2400) and 5140 (do.: about 4000) (products of Rika-Hercules Inc.). These styrenic oligomers are desirably used in an amount of 0.5 to 10% by weight based on the styrenic thermoplastic elastomer used as the base material.

Further, additives which can be used if necessary, in addition to the above-described indispensable components, such as a resin, filler, stabilizer, colorant, and antifungal and antimicrobial agent are similar to those described above with reference to the first embodiment. Also oily matters such as petroleum oils and liquid polymers used in the first embodiment are usable in a suitable amount as a constituent of the eraser of the second embodiment. The eraser can be produced by the same method as that described with reference to the first embodiment.

As described above, in the eraser of the second embodiment of the present invention, the styrenic oligomer is incorporated into the styrene domain in each elastomer used as the base material to reduce the average molecular weight of the polystyrene in the domain to thereby reduce the strength of the domain and to achieve an excellent erasing performance even when it is used under a weak rubbing force. Other effects of the eraser are that the textures of the abrasion surface of the eraser and the refuse thereof are fined, that a pleasant touch is realized during the use and that the feeling of a higher grade of the eraser can be realized.

Finally, a description will be made on the eraser of the third embodiment of the present invention which comprises an olefinic thermoplastic elastomer as the base material and which has a number of microvoids therein.

The olefinic thermoplastic elastomers to be used as the base material are roughly classified into copolymeric, simple blend, partially crosslinked and completely crosslinked thermoplastic elastomers. Among them, preferred are partially or completely crosslinked thermoplastic elastomers disclosed in Japanese Patent Publication Nos. 21021/1978 and 34210/1978 and U.S. Patent Nos. 4,104,210 and 4,130,535. In these partially or completely crosslinked thermoplastic elastomers, the relative amount of the rubber component to the whole elastomer can be increased, since the rubber component in the elastomer is partially or completely crosslinked and, as a result, the elasticity of the elastomer becomes closer to that of an ordinary crosslinked rubber. From the viewpoint of the quality of the eraser, the resultant eraser is preferably one which is soft and has an elasticity close that of the crosslinked rubber, in particular, one having a rubber hardness of 85 or below (JIS K 6301; with A type hardness meter; the sample being one produced by molding the elastomer at a temperature higher than the melting point of the molecule-constraining component).

Also the olefinic thermoplastic elastomer has a molecule-constraining component (hard segment) for preventing the molecule from causing plastic deformation and an elastic rubber component (soft segment) in its structure. The molecule-constraining components include highly crystalline polyethylene and polypropylene, and the rubber components include ethylene/propylene copolymer rubber and ethylene/propylene/nonconjugated diene terpolymer rubber. In such an olefinic thermoplastic elastomer, the domain comprising the molecule-constraining components is plasticized to lose the power of constraining the molecules at the melting point of the molecule-constraining component (for example, polypropylene: 170°C, and polyethylene: 100 to 140°C) or above. Thus the olefinic thermoplastic elastomer has properties of the vulcanized rubber at ambient temperature and it can be molded on an ordinary plastic molding machine at a high temperature (usually 200°C or above).

Examples of the commercially available olefinic thermoplastic elastomers includes Sumitomo TPE 3570, 3680, 3780 and 3385 (products of Sumitomo Chemical Co., Ltd.); Nisseki Softrex EL8AT21, EL7AT21 and EL6AT21 (products of Nippon Petrochemical Co., Ltd.); Santoprene 101-55, 101-64, 101-80, 201-55, 201-64, 201-73 and 301-87 (products of Monsanto Japan Ltd.); Milastomer 5030N, 6030N, 7030N and 8032N and Goodmer S500 (products of Mitsui Petrochemical Industries, Ltd.); and Thermorun 3550, 3650 and 3061 (products of Mitsubishi Petrochemical Co., Ltd.).

The eraser comprising the olefinic thermoplastic elastomer as the base material must have a number of microvoids therein. When the molding is conducted at an ordinary molding temperature of 200°C or above, a number of microvoids are not formed in the eraser and the breaking strength of the olefinic thermoplastic elastomer per se is still high and the eraser is not abraded by rubbing to make the use thereof as the eraser impossible.

For forming a number of microvoids in the eraser comprising the olefinic thermoplastic elastomer as the base material, a process can be employed wherein the materials are kneaded by a shearing force with a two-roller mill at a temperature not above the melting point of the molecule-constraining component in the elastomer and then the kneaded mixture is molded by an ordinary method such as pressing. The kneading temperature is preferably 150°C or below when the molecule-constraining component is polypropylene, and is preferably 80°C or below when it is polyethylene. Further, the kneading temperature is preferably room temperature to 50°C irrespective of the molecule-constraining component.

If necessary, chlorine-free thermoplastic resins other than the olefinic thermoplastic elastomers, and styrenic, ester and urethane thermoplastic elastomers can be used in addition to the above-described indispensable components. Further, additives ordinarily contained in erasers, such as a filler, stabilizer, colorant and antifungal and antimicrobial agent are suitably usable. The fillers include calcium carbonate, magnesium carbonate, diatomaceous earth, clay, and fibrous and needle-like fillers for improving the bending strength, such as potassium titanate fibers, magnesium sulfate fibers, silicon nitride whiskers and silicon carbide whiskers. The stabilizers include antioxidants such as hindered phenols, ultraviolet absorbers such as benzotriazoles and oxalic acid anilides, and ultraviolet stabilizers such as hindered amines. The colorants include organic and inorganic pigments. The antifungal and antimicrobial agents include 2-(4-thiazolyl)-benzimidazole, zinc 2-pyridinethiol-1-oxide, metallic silver supported by calcium phosphate carrier and zinc antimicrobial agents.

As described above, the eraser of the third embodiment can be produced by kneading the above-described components by a shearing force on an ordinary mixer such as a two-roller mill at a temperature lower than the melting point of the molecule-constraining component in the olefinic thermoplastic elastomer and then molding the resultant mixture on a pressing machine.

In the eraser of the third embodiment of the present invention as described above, the olefinic thermoplastic elastomer used as the base material has an island-sea-structure wherein the domains of the molecule-constraining components are present like islands in the sea of the rubber component. Since the rubber components in the form of small particles are crosslinked, the whole does not form together a matrix but it is an aggregate of small matrixes. Further, in the course of the crosslinking of the rubber component, it is partially grafted with the molecule-constraining component and, therefore, the rubber component constituting the small matrix is constrained by the domain of the molecule-constraining component. When the kneading is conducted at the melting point of the domain of the molecule-constraining component or below, the domain remains as it is to cause a shear among the rubber component particles. It is supposed, therefore, that the eraser of the third embodiment of the present invention comprises an aggregate of rubber component particles each comprising a molecule-constraining component as the nucleus, which is surrounded by the rubber component, and that the eraser has a number of microvoids formed therein and is easily abraded by rubbing.

The following Examples will further illustrate the present invention.

Example 1

Styrenic thermoplastic elastomers:	
"Cariflex TR1101"	35 parts by weight
"Kraton G1726X"	15 parts by weight
paraffinic oil "DIANA PW-380"	60 parts by weight
filler: heavy calcium carbonate	100 parts by weight
stabilizer "IRGANOX 1010" (CIBA-GEIGY Limited, Germany)	1 part by weight
gelling agent: fine silica powder "Aerosil #200" (Nippon Aerosil Co., Ltd.)	0.6 part by weight

Among the above-mentioned components, the two kinds of styrenic thermoplastic elastomers were thoroughly kneaded on a two-roller mill heated to 120°C. A gel previously prepared by mixing the paraffinic oil and the gelling agent, and the other components were added to the resultant mixture, and the mixture thus obtained was further kneaded. After the completion of the kneading, the obtained mixture was fed into a mold and pressed at 120°C for 10 min. to obtain a block-shaped eraser.

Example 2

5	Styrenic thermoplastic elastomers:	
	"Septon 2002"	50 parts by weight
	"Asaprene T-430"	100 parts by weight
	naphthenic oil "DIANA NS-24"	300 parts by weight
	filler: heavy calcium carbonate	200 parts by weight
10	stabilizer "IRGANOX 1010"	1 part by weight
	gelling agent: fine silica powder "Nipsil LP" (Nippon Silica Industrial Co., Ltd.)	9 parts by weight

Among the above-mentioned components, the two kinds of styrenic thermoplastic elastomers were thoroughly kneaded on a two-roller mill heated to 120°C. A gel previously prepared by mixing the naphthenic oil and the gelling agent, and the other components were added to the resultant mixture, and the mixture thus obtained was further kneaded. After the completion of the kneading, the obtained mixture was fed into a mold and pressed at 120°C for 10 min. to obtain a block-shaped eraser.

Example 3

25	Styrenic thermoplastic elastomer:	
	"Solprene T-475" (mixture of 50 parts by weight of triblock copolymer and 25 parts by weight of naphthenic oil)	75 parts by weight
	Olefinic thermoplastic elastomer "Milastomer 7030N"	50 parts by weight
	filler: heavy calcium carbonate	100 parts by weight
	naphthenic oil "DIANA NU-80"	50 parts by weight
30	Stabilizer "IRGANOX 1010"	1 part by weight
	gelling agent: dibenzylidenesorbitol "GELALL D" (New Japan Chemical Co., Ltd.)	0.5 part by weight

Among the above-mentioned components, the two kinds of thermoplastic elastomers were thoroughly kneaded on a two-roller mill heated to 120°C. A gel previously prepared by mixing the naphthenic oil and the gelling agent under heating to once obtain a solution and then cooling it, and the other components were added to the resultant mixture, and the mixture thus obtained was further kneaded. After the completion of the kneading, the obtained mixture was fed into a mold and pressed at 120°C for 10 min. to obtain a block-shaped eraser.

Example 4

45	Styrenic thermoplastic elastomers:	
	"Cariflex TR1101"	35 parts by weight
	"Kraton G1726X"	15 parts by weight
	liquid polymer: "Nisseki"	60 parts by weight
	Polybutene LV-50" filler: heavy calcium carbonate	100 parts by weight
50	stabilizer "IRGANOX 1010"	1 part by weight
	gelling agent: dextrin palmitate "Rheopearl KE" (Sansho Co., Ltd.)	0.3 part by weight

Among the above-mentioned components, the two kinds of styrenic thermoplastic elastomers were thoroughly kneaded on a two-roller mill heated to 120°C. A gel previously prepared by mixing the liquid polymer and the gelling agent under heating to obtain a solution and then cooling it, and the other components were added to the resultant mixture, and the mixture thus obtained was further kneaded. After the completion of the kneading, the obtained mixture was fed into a mold and pressed at 120°C for 10 min. to obtain a block-shaped eraser.

Example 5

5	Styrenic thermoplastic elastomer:	
	"Septon 2002"	50 parts by weight
	liquid polymer: "Nisseki Polybutene HV-15"	100 parts by weight
	filler: heavy calcium carbonate	200 parts by weight
	stabilizer "IRGANOX 1010"	1 part by weight
10	gelling agent: bentonite	5 parts by weight
	liquid paraffin "DN. Oil KP32" (Idemitsu Kosan Co., Ltd.)	36 parts by weight

15 Among the above-mentioned components, the styrenic thermoplastic elastomer and liquid paraffin were thoroughly kneaded on a two-roller mill heated to 120 °C. A gel previously prepared by mixing the liquid polymer and the gelling agent, and the other components were added to the resultant mixture, and the mixture thus obtained was further kneaded. After the completion of the kneading, the obtained mixture was fed into a mold and pressed at 120 °C for 10 min. to obtain a block-shaped eraser.

Example 6

20	Styrenic thermoplastic elastomer:	
	"Solprene T-406"	50 parts by weight
25	olefinic thermoplastic elastomer "Milastomer 7030N"	50 parts by weight
	filler: heavy calcium carbonate	100 parts by weight
	liquid polymer "Idemitsu Polybutene OR"	75 parts by weight
	stabilizer "IRGANOX 1010"	1 part by weight
30	gelling agent: "Aerosil #200"	1.5 parts by weight

35 Among the above-mentioned components, the two kinds of thermoplastic elastomers were thoroughly kneaded on a two-roller mill heated to 120 °C. A gel previously prepared by mixing the liquid polymer and the gelling agent, and the other components were added to the resultant mixture, and the mixture thus obtained was further kneaded. After the completion of the kneading, the obtained mixture was fed into a mold and pressed at 120 °C for 10 min. to obtain a block-shaped eraser.

Example 7

40	Styrenic thermoplastic elastomers:	
	"Solprene T-406"	27 parts by weight
	"Kraton G1650"	18 parts by weight
45	olefinic thermoplastic elastomer:	
	"Softrex D9010" (copolymer, Nippon Petrochemical Co., Ltd.) styrenic oligomer	9 parts by weight
	"Kristalex 3100"	1.4 parts by weight
50	liquid paraffin "DN. Oil KP32"	36 parts by weight
	filler: heavy calcium carbonate	100 parts by weight
	stabilizer "IRGANOX 1010"	0.5 part by weight

55 The above-mentioned components were thoroughly kneaded on a two-roller mill. The mixture thus obtained was molded on an extruder to obtain an eraser.

Example 8

5

10

Styrenic thermoplastic elastomers:	
"Cariflex TR1101"	27 parts by weight
"Kraton G1652"	9 parts by weight
"Septon 2043"	18 parts by weight
Styrenic oligomer: "Piccolastic A75"	4.5 parts by weight
liquid polybutene	27 parts by weight
filler: heavy calcium carbonate	80 parts by weight
stabilizer "IRGANOX 1010"	0.5 part by weight

15

The above-mentioned components were thoroughly kneaded on a two-roller mill. The mixture thus obtained was molded on an extruder to obtain an eraser.

Example 9

20

25

Olefinic thermoplastic elastomer:	
"Santoprene 201-55" (rubber hardness: 55, molecule-constraining component: polypropylene [m.p.: about 170 ° C])	100 parts by weight

30

The above-mentioned component was thoroughly kneaded on a two-roller mill at room temperature. After the completion of the kneading, it was fed into a mold and pressed at room temperature for 10 min. to obtain a block-shaped eraser.

Example 10

35

Olefinic thermoplastic elastomer:	
"Milastomer 6030N" (rubber hardness: 60, molecule-constraining component: polypropylene [m.p.: about 170 ° C])	100 parts by weight

40

The above-mentioned component was thoroughly kneaded on a two-roller mill at room temperature. After the completion of the kneading, it was fed into a mold and pressed at room temperature for 10 min. to obtain a block-shaped eraser.

45

Example 11

50

55

Olefinic thermoplastic elastomer:	
"Sumitomo TPE3780" (rubber hardness: 66, molecule-constraining component: polypropylene [m.p.: about 170 ° C])	100 parts by weight
filler: heavy calcium carbonate	10 parts by weight
stabilizer: "IRGANOX 1010"	1 part by weight
pigment: titanium oxide	2 parts by weight

The above-mentioned components were thoroughly kneaded on a two-roller mill at 120 ° C. After the completion of the kneading, the mixture was fed into a mold and pressed at 120 ° C for 10 min. to obtain a

block-shaped eraser.

Example 12

5

10

Olefinic thermoplastic elastomer:	
"Thermorun 3650" (rubber hardness: 65, molecule-constraining component: polypropylene [m.p.: about 170 °C])	100 parts by weight
filler: heavy calcium carbonate	10 parts by weight
stabilizer "IRGANOX 1010"	1 part by weight
pigment: titanium oxide	2 parts by weight

15

The above-mentioned components were thoroughly kneaded on a two-roller mill at 100 °C. After the completion of the kneading, the mixture was fed into a mold and pressed at 100 °C for 10 min. to obtain a block-shaped eraser.

Comparative Example 1 [comparison with Example 1]

20

25

Styrenic thermoplastic elastomers:	
"Cariflex TR1101"	35 parts by weight
"Kraton G1726X"	15 parts by weight
paraffinic oil "DIANA PW-380"	175 parts by weight
filler: heavy calcium carbonate	100 parts by weight
stabilizer "IRGANOX 1010"	1 part by weight

30

Among the above-mentioned components, the two kinds of styrenic thermoplastic elastomers were thoroughly kneaded on a two-roller mill heated to 120 °C. The other components were added to the resultant mixture, and the mixture thus obtained was further kneaded. After the completion of the kneading, the obtained mixture was fed into a mold and pressed at 120 °C for 10 min. to obtain a block-shaped eraser.

35

Comparative Example 2 [comparison with Example 1]

40

45

Styrenic thermoplastic elastomers:	
"Cariflex TR1101"	35 parts by weight
"Kraton G1726X"	15 parts by weight
paraffinic oil "DIANA PW-380"	175 parts by weight
filler: heavy calcium carbonate	350 parts by weight
stabilizer "IRGANOX 1010"	1 part by weight

50

Among the above-mentioned components, the two kinds of styrenic thermoplastic elastomers were thoroughly kneaded on a two-roller mill heated to 120 °C. Then the same procedure as that of Comparative Example 1 was repeated to obtain an eraser.

55

Comparative Example 3 [comparison with Example 7]

5	Styrenic thermoplastic elastomers:	
	"Solprene TR-406"	27 parts by weight
	"Kraton G1650"	18 parts by weight
	Olefinic thermoplastic elastomer: "Softrex D9010" (copolymer, Nippon Petrochemical Co., Ltd.)	9 parts by weight
10	liquid paraffin "DN. Oil KP32"	36 parts by weight
	filler: heavy calcium carbonate	100 parts by weight
	stabilizer "IRGANOX 1010"	0.5 parts by weight

15 An eraser was produced from the above-described components in the same manner as that of Example 7.

Comparative Example 4 [comparison with Example 8]

20	Styrenic thermoplastic elastomers:	
	"Cariflex TR1101"	27 parts by weight
	"Kraton G1652"	9 parts by weight
	"Septon 2043"	18 parts by weight
25	liquid polybutene	27 parts by weight
	filler: heavy calcium carbonate	80 parts by weight
	stabilizer "IRGANOX 1010"	0.5 part by weight

30 An eraser was produced from the above-described components in the same manner as that of Example 8.

Comparative Example 5 [comparison with Example 10]

35	Olefinic thermoplastic elastomer:	
40	"Milastomer 6030N" (rubber hardness: 60, molecule-constraining component: polypropylene [m.p.: about 170 °C])	100 parts by weight

45 An eraser was produced in the same manner as that of Example 10 except that each of the kneading and pressing temperatures was altered to 220 °C which is higher than the melting point of the polypropylene.

Comparative Example 6 [comparison with Example 12]

50	Olefinic thermoplastic elastomer:	
	"Thermorun 3650" (rubber hardness: 65, molecule-constraining component: polypropylene [m.p.: about 170 °C])	100 parts by weight
	filler: heavy calcium carbonate	10 parts by weight
55	stabilizer "IRGANOX 1010"	1 part by weight
	pigment: titanium oxide	2 parts by weight

An eraser was produced in the same manner as that of Example 12 except that each of the kneading and pressing temperatures was altered to 220°C which is higher than the melting point of the polypropylene.

5 Comparative Example 7 [conventional polyvinyl chloride eraser]

Polyvinyl chloride resin:	
"ZEON 121" (NIPPON ZEON Co., Ltd.) plasticizer: dioctyl phthalate stabilizer: epoxidized soybean oil filler: heavy calcium carbonate	30 parts by weight 35 parts by weight 0.6 part by weight 35 parts by weight

15 The above-mentioned components were mixed together to obtain a paste, which was fed into a mold and pressed at 110°C for 20 min. to obtain a conventional polyvinyl chloride eraser.

Examples 1 through 6 relate to the eraser of the first embodiment of the present invention. Comparative Examples 1 and 2 are given for the comparison therewith. Comparative Example 7 relates to the conventional polyvinyl chloride eraser.

20 The rate of erasure was determined according to JIS S 6050 with each of the erasers obtained in Examples 1 to 6 and Comparative Examples 1, 2 and 7. The rate of erasure of each of the erasers obtained in Examples 1 to 6 was at least 80%, which satisfied the JIS specification.

Then the erasing performance achieved by applying each of the erasers obtained in Examples 1 to 6 with a hand under a weak rubbing force was compared with that of the conventional polyvinyl chloride eraser obtained in Comparative Example 7 to find that they were equal.

After the erasers were kept in a sealed vessel for 3 months, no blooming phenomenon occurred and the erasing performance was not deteriorated in the erasers obtained in Examples 1 to 6, while the blooming phenomenon occurred in the gelling-agent-free eraser obtained in Comparative Example 1 to stain the paper surface and the user's hand. When the eraser obtained in Comparative Example 2 was used, the colorant in the handwriting could not be incorporated into the refuse of the eraser, and the paper surface was stained black, though the blooming phenomenon did not occur, since a large amount of the filler was incorporated in place of the gelling agent in order to inhibit the blooming phenomenon.

Examples 7 and 8 relate to the eraser of the second embodiment of the present invention. Comparative Examples 3 and 4 are given for the comparison therewith.

35 The rate of erasure was determined according to JIS S 6050 with each of the erasers obtained in Examples 7 and 8 and Comparative Examples 3 and 4. The rate of erasure of each of the erasers obtained in Examples 7 and 8 was at least 80%, which satisfied the JIS specification.

Then the erasing performance achieved by applying each of the erasers obtained in Examples 7 and 8 with a hand under a weak rubbing force was compared with that of the conventional polyvinyl chloride eraser obtained in Comparative Example 7 to find that they were equal.

40 The erasers obtained in Examples 7 and 8 had smooth and good-looking erasing surfaces and a smooth feeling was realized by rubbing with them. On the contrary, when the styrenic-oligomer-free erasers obtained in Comparative Examples 3 and 4 were used, the paper surface rubbed with them was coarsened and stained, though the rate of erasure was above 80%. The feel of the erasers in use was such that the erasers were crumbled into large masses and rolled about on the paper surface.

Examples 9 to 12 relate to the eraser of the third embodiment of the present invention. Comparative Examples 5 and 6 are given for the comparison therewith.

50 The inside of each of the erasers obtained in Examples 9 to 12 and Comparative Examples 5 and 6 was observed at x1000 magnification under a scanning electron microscope to confirm a number of microvoids in the erasers obtained in the Examples, while the erasers obtained in the Comparative Examples had a substantially homogeneous section and no voids were recognized therein.

55 The rate of erasure was determined according to JIS S 6050 with each of the erasers obtained in Examples 9 to 12 and Comparative Examples 5 and 6. The rate of erasure of each of the erasers obtained in Examples 9 to 12 was at least 80%, which satisfied the JIS specification. On the contrary, when the erasers obtained in Comparative Examples 5 and 6 were used, no refuse was formed, since the erasers were not abraded, and the paper surface was stained black, though the carbon powder forming handwriting was adsorbed.

Then the erasing performance achieved by applying each of the erasers obtained in Examples 9 to 12 with a hand under a weak rubbing force was compared with that of the conventional polyvinyl chloride eraser obtained in Comparative Example 7 to find that they were equal.

As described above in detail, the eraser of the present invention can be incinerated without emitting any toxic chlorine-containing gas, since no chlorine-containing compound is used as the starting material and, in addition, it is excellent in erasing performance even when applied under a weak rubbing force like the conventional polyvinyl chloride eraser.

Claims

10

1. An eraser comprising a styrenic thermoplastic elastomer as a base material, 1 to 3 parts by weight, per part by weight of the base material, of an oily matter and a gelling agent.

15

2. The eraser according to Claim 1, wherein the styrenic thermoplastic elastomer is one or a mixture of two or more triblock copolymers selected from among styrene/butadiene/styrene copolymer, styrene/isoprene/styrene copolymer, styrene/ethylenbutylene/styrene copolymer and styrene/ethylenepropylene/styrene copolymer.

20

3. The eraser according to Claim 1 or 2, wherein the oily matter is petroleum oil.

4. The eraser according to Claim 3, wherein the petroleum oil is one or a mixture of two or more oils selected from among liquid paraffin, paraffinic oils and naphthenic oils.

25

5. The eraser according to Claim 1 or 2, wherein the oily matter is a liquid polymer.

6. The eraser according to Claim 5, wherein the liquid polymer is one or a mixture of two or more oils selected from among liquid polyisoprene, liquid polybutadiene and liquid polybutene.

30

7. The eraser according to any of Claims 1 to 6, wherein the gelling agent is used in an amount of 0.1 to 10% by weight based on the oily matter.

8. The eraser according to any of Claims 1 to 7, wherein the gelling agent is an organic one.

35

9. The eraser according to Claim 8, wherein the organic gelling agent is one or a mixture of two or more gelling agents selected from among dibenzylidenesorbitol, tribenzylidenesorbitol and dextrin/fatty acid esters.

10. The eraser according to any of Claims 1 to 7, wherein the gelling agent is an inorganic one.

40

11. The eraser according to Claim 10, wherein the inorganic gelling agent is one or a mixture of two or more gelling agents selected from among silica and bentonite.

12. The eraser according to any of Claims 1 to 11, which further contains a styrenic thermoplastic elastomer comprising a diblock copolymer as the base material.

45

13. An eraser comprising a styrenic thermoplastic elastomer as a base material and a styrenic oligomer.

50

14. The eraser according to Claim 13, wherein the styrenic thermoplastic elastomer is one or a mixture of two or more triblock copolymers selected from among styrene/butadiene/styrene copolymer, styrene/isoprene/styrene copolymer, styrene/ethylenbutylene/styrene copolymer and styrene/ethylenepropylene/styrene copolymer.

15. The eraser according to Claim 13 or 14, wherein the styrenic oligomer is used in an amount of 0.5 to 10% by weight based on the styrenic thermoplastic elastomer.

55

16. The eraser according to any of Claim 13 to 15, wherein the styrenic oligomer is one or a mixture of two or more oligomers selected from among polystyrene, styrene/acrylic copolymers and α -methylstyrene.

17. An eraser comprising an olefinic thermoplastic elastomer as a base material, and having a number of microvoids therein.

5 18. The eraser according to Claim 17, wherein the olefinic thermoplastic elastomer is partially crosslinked or wholly crosslinked.

19. The eraser according to Claim 17 or 18, wherein the olefinic thermoplastic elastomer has a rubber hardness of 85 or below.

10 20. The eraser according to any of Claims 17 to 19, wherein the olefinic thermoplastic elastomer has a molecule-constraining component and a rubber component in its structure, and the eraser being prepared by kneading and molding at a temperature not higher than the melting point of the molecule-constraining component.

15

20

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00239

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁵ B43L19/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁵ B43L19/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1961 - 1992

Kokai Jitsuyo Shinan Koho 1971 - 1992

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 1-105799 (Pentel K.K.), April 24, 1989 (24. 04. 89), (Family: none) Line 17, lower right column, page 2 to line 16, upper right column, page 3	1-16
Y	JP, A, 56-127498 (J.S. Staedtler), October 6, 1981 (06. 10. 81), & DE, C2, 3005298 & US, A, 4350787 Lines 11 to 17, lower right column, page 1	1, 3, 4
Y	JP, B2, 58-52520 (Pentel K.K.), November 22, 1983 (22. 11. 83), & US, A, 4268411 & DE, A1, 2912442 & FR, A1, 2420994 & GB, A, 2019805 Lines 2 to 25, right column, page 3	1, 5-7, 13, 15, 16
	JP, A, 1-259999 (Daito Kako K.K.), October 17, 1989 (17. 10. 89), & US, A, 5055947	

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

-A- document defining the general state of the art which is not considered to be of particular relevance

-E- earlier document but published on or after the international filing date

-L- document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

-O- document referring to an oral disclosure, use, exhibition or other means

-P- document published prior to the international filing date but later than the priority date claimed

-T- later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

-X- document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

-Y- document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

-A- document member of the same patent family

Date of the actual completion of the international search

May 13, 1993 (13. 05. 93)

Date of mailing of the international search report

June 1, 1993 (01. 06. 93)

Name and mailing address of the ISA/

Japanese Patent Office

Facsimile No.

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00239

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Line 18, lower left column to line 4, lower right column, page 2 JP, A, 2-41298 (Pentel K.K.), February 9, 1990 (09. 02. 90), (Family: none)	1, 7-11
Y	Line 19, upper right column to line 7, lower left column, page 3	17-20.
Y	Line 4, lower left column to line 20, lower right column, page 4 JP, A, 2-111598 (Pentel K.K.), April 24, 1990 (24. 04. 90), (Family: none)	17, 20
Y	Line 9, upper left column to line 3, upper right column, page 2	19